

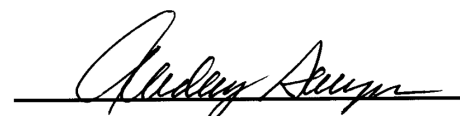
# ANALYSIS OF LEGACY PHOSPHOROUS IN AGRICULTURAL DRAINAGE DITCHES OF THE LAKE ERIE WATERSHED

Undergraduate Research Thesis  
Submitted in partial fulfillment of the requirements for graduation  
with research distinction in Earth Sciences  
in the undergraduate colleges of  
The Ohio State University

By

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2018

Approved by

A handwritten signature in black ink, appearing to read "Audrey Sawyer", is written over a solid horizontal line.

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## **TABLE OF CONTENTS**

Abstract.....	ii
Acknowledgements.....	iii
List of Figures.....	iv
Introduction.....	1
Site Description.....	2
Methods	
Sampling Methods.....	3
Sediment Analyses.....	4
Results.....	5
Discussion.....	10
Conclusion.....	13
Recommendations for Future Research.....	14
References Cited.....	15
Appendix.....	17

## **ABSTRACT**

Agricultural best management practices have reduced the total phosphorous (P) being delivered to Lake Erie for almost 40 years, yet the proportion of bioavailable P (soluble reactive phosphorous, SRP) has steadily increased, contributing to harmful algal blooms. A possible continuous source of P to Lake Erie is sediment in agricultural drainage ditches, which contains SRP in pore waters, as well as sorbed P that can be released due to changes in redox conditions. Physical sediment properties and P content were analyzed in ten cores collected during the spring of 2018 from two agricultural drainage ditches in the Lake Erie watershed. These spring cores were compared to summer cores that were collected at the end of the previous growing season from the same locations. A two-step extraction process designed to measure loosely sorbed P and P sorbed to redox-sensitive iron and manganese oxides was utilized to determine concentrations of P. On average, the concentration of P sorbed to redox-sensitive metal oxides was an order of magnitude greater than loosely sorbed P, demonstrating the potential importance of metal oxidation state in the mobility of P. Overall P content was greater in summer cores. Seasonal changes could be due to agricultural practices such as fertilizer application or more natural changes in aquatic plant growth and flow within ditches. Stagnant summertime flow and an abundance of organic matter could drive anoxic conditions in pore water and mobilize P associated with redox-sensitive metal oxides. One site consistently had greater P concentrations across both seasons, but P concentration also varied strongly within sites. Cores with more organic matter tended to have greater P content. Overall, these results suggest that variations in hydrology and sediment composition could influence hot spots of P retention and release throughout the watershed.

## **ACKNOWLEDGEMENTS**

Many thanks to Ohio Sea Grant and to Shell Exploration and Production Company for their generous funding of this project.

Thanks also to: Dr. Audrey Sawyer, my professor and thesis advisor, for her help and support from the first papers read before entering the field until the last test run and final paper edits and everything in between. Dr. Nadia Casillas, for her expertise in analytical chemistry and hard work and dedication in seeing the lab process through and leading the charge. Kelsey Danner, for laying the groundwork for the entire project and completing the original summer cores and streamlining the process in doing so. Amelia Nelson, for spending a day in the drainage ditches with me and laboring and persisting to obtain the sediment cores. I also thank Dr. Mike Wilkins and his laboratory group for allowing us to use their space and equipment. Deon Knights, Corey Wallace, and Dr. Sue Welch provided valuable training in grain size analysis and loss on ignition. Thanks also to Dr. Anne Carey for her support and experience in developing and fine-tuning the written results and presentation, as well as to her and Dr. Derek Sawyer for their mentoring in the Shell Undergraduate Research Program (SURE) over the summertime.

Special thanks to Drs. Kevin King and Brittany Hanrahan at the USDA for sharing their knowledge and expertise and for allowing us to use their agricultural drainage sites and collaborating on the project.

Thanks also to The Ohio State University and the School of Earth Sciences for providing the access to this amazing opportunity.

Finally, thank you to my family and especially my wonderful parents, Doug and Bethany Covault, for always being there for me and pushing me to see everything through to the end and giving my best.

## **LIST OF FIGURES**

1. Aerial Photographs of Field Sites
2. Core Location Maps
3. Photograph of Coring Process
4. Physical Sediment Properties
  - a) Wet-Weight Dry-Weight Ratios
  - b) Loss on Ignition
5. Loosely Bound Phosphorous
6. Phosphorous in Porewater vs Loosely Bound Phosphorous in Sediments
7. Loosely Bound Phosphorous vs Loss On Ignition
8. Phosphorous Bound to Redox Sensitive Iron and Manganese
9. Phosphorous Bound to Redox-Sensitive Fe/Mn vs Loss On Ignition
10. Cartoon of Agricultural Drainage Ditch Cross-Section

## INTRODUCTION

Since the 1960s eutrophication and harmful algae blooms (HABs) have plagued the Great Lakes, particularly Lake Erie (Michalak et al., 2013). HABs are not only harmful to the health of Lake Erie and its biota but also create challenges for drinking water treatment and harm economies such as tourism. Some blue-green algae can produce a toxin called microcystin, which causes serious gastrointestinal distress and liver harm in humans and has been responsible for the death of smaller animals such as dogs (Ohio EPA, 2015).

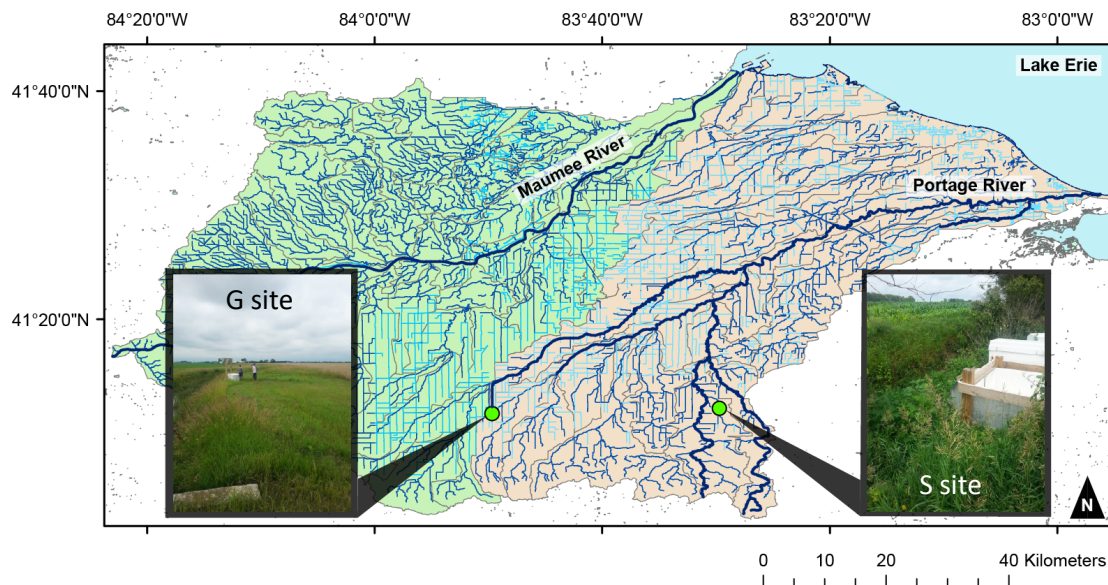
Excess nutrients are a major cause of HABs in Lake Erie. In particular, phosphorous, which is usually the primary limiting nutrient in inland water systems, has been exported to the lake in great excess (International Joint Commission, 2014). While particulate loads of P to Lake Erie have decreased thanks to the implementation of best management practices (BMPs), dissolved P loads have continued to increase (Jarvie et al., 2013). BMPs target particulate P because it has historically been thought that dissolved P will sorb to the sediments or be taken up by vegetation and not be exported to Lake Erie (Penn et al., 2014). Yet particulate P is not immediately bioavailable to cyanobacteria, while dissolved P is highly bioavailable (Richards et al., 2010).

A large fraction of the annual P load delivered to Lake Erie is associated with base flow contributions from rivers, which ultimately originate from groundwater discharge (Algoazany et al., 2007; Novak et al., 2003). This observation suggests that dissolved P can be mobilized, depending on sediment and pore water chemistry (Holman et al., 2008; Spiteri et al., 2007). The interface between aquifers and streams where groundwater discharge occurs has steep gradients in redox potential and redox-sensitive solutes such as dissolved iron (Fe) and manganese (Mn) (Carlyle and Hill, 2001). As Fe-rich groundwater mixes with oxygenated surface water, iron oxides can precipitate near the sediment-water interface and sequester P from both surface water and groundwater (Hendricks and White, 2000; Carlyle and Hill, 2001). Oxidation of organic carbon deposited on streambeds can also lead to reduction of Fe-oxides and mobilization of P (Hunter et al., 1998; Shuttleworth et al., 1999). These changes in redox conditions are likely to occur over short and long timescales, but particularly over the growing season as the growth of aquatic vegetation restricts flow in ditches, promoting anoxic conditions and reduction of iron oxides across spring and summer. P that has previously been considered sequestered in the sediments is termed legacy P. Seasonal release of legacy P from agricultural drainage ditches may contribute to the growing dissolved P loads to Lake Erie (Jarvie et al., 2013; Penn, et al., 2014; Sharpley et al., 2013).

To assess the potential for sediments in agricultural drainage ditches to release legacy P, I collected spring core samples from two unnamed tributaries (agricultural drainage ditches) within Wood County, Ohio. Summer cores from these same locations had previously been collected by Kelsey Danner at the end of the previous growing season. The sites are located in the Cedar-Portage Watershed, which drains to Western Lake Erie. I completed a two-step phosphorus extraction on core samples and characterized their physical properties (organic matter, via loss on ignition, and wet-weight dry-weight ratio) to understand the fractions of more mobile P and their relation to sediment properties. I also compared my results with the results from summer cores to examine changes through time. I show that, on average, P content is almost twice the content in summertime cores than spring cores, but large variations occur between sites and over small scales within sites.

## SITE DESCRIPTION

The agricultural drainage ditches selected for this study were the S site and G site in the Cedar-Portage Watershed (HUC 04100010) within the Western Lake Erie basin (**Figure 1**). The sites were chosen because they are the focus of additional edge-of-field research estimating P loads from tile drainage and run-off funded through a USDA grant to Kevin King. They have a similar, predominantly agricultural upstream land use. The ditches are approximately 2 m wide, 2 m deep, and are separated from crop fields by grass buffer zones that are 5 and 10 m wide at S and G sites, respectively. Flow depths and velocities in the ditches are largely dependent on precipitation events. Observed water level and flow tends to be greater in spring (April through June) and lower in late summer and early fall (August through October). Seasonal algal mats are common at the S site, which has some shading from the canopy. Dense aquatic vegetation is common in summer at the G site, which lacks canopy. Surficial bed materials at both sites are composed of mixed gravel and silt. Compacted glacial till lies approximately 10 cm beneath the sediment-water interface.

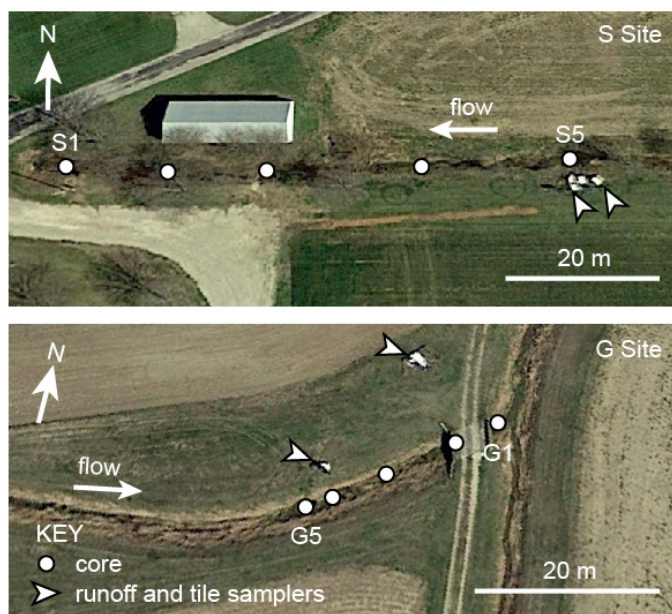


**Figure 1.** Study sites (green dots) are located at agricultural drainage ditches in the Portage River watershed (orange). Rivers and streams are shown in dark blue. Canals and drainage ditches are shown in light blue. Inset photos depict existing site infrastructure, which includes flumes and automated samplers.



## METHODS

**Sediment Collection.** At each site, five sediment cores were collected on May 29th, 2018 (numbered from downstream to upstream). The fifth core at each site was located immediately beneath the outflow for a tile drain where an autosampler was installed by the USDA (**Figure 2**). The length from the first to last core was approximately 60 m at the S site and 30 m at the G site. Core collection methods and locations were the same as summertime sampling by Kelsey Danner, which occurred on August 29th, 2017.



**Figure 2.** Maps of S and G site showing site orientations, locations of cores, USDA tile samplers, and direction of flow.

Cores were collected using a mallet to drive two-inch diameter, six-inch-long, clear PVC core liners into the sediment bed to the depth of refusal (typically 10 to 20 cm at each location). A cap was placed on top of the core liner to preserve the overlying water column. Cores were then extracted using a trowel and immediately capped on the bottom to minimize sediment loss and disturbance. Cores and their overlying surface water were tightly sealed with tape, placed on ice in upright positions, and transported back to The Ohio State University for analysis within 24 hours.



**Figure 3.** Photograph of core collection at the more densely vegetated G site in spring of 2018. Care was taken to capture representative roots and organic matter.

**Pore water collection.** Within 24 hours of arrival at Ohio State (or 36 hours of core retrieval), pore water was collected from all ten cores using Rhizon CSS samplers (0.15  $\mu\text{m}$  pore size, 5 cm length). The upper cap was removed as the sediments were still protected from changes in redox conditions by the overlying surface water. Then, rhizons were inserted vertically into each core until the filters were completely submerged in the sediment to ideally draw from the pore water and not the surface water. Rhizons were then attached to 20mL Luer-Lok syringes and plungers were pulled fully back and then held open to maintain a vacuum using wooden shims until a minimum of 10mL of samples was extracted. Pore water samples were immediately acidified with 1 M  $\text{H}_2\text{SO}_4$  (2% by volume) and analyzed for soluble reactive phosphorus (SRP) within 2 weeks following the ascorbic acid method (APHA, 1985).

**Sediment properties.** Cores were transferred to an anaerobic glove box (95%  $\text{N}_2$  and 5%  $\text{H}_2$ ), where the overlying water was removed with a syringe. The upper 5 cm of sediment was then transferred from each core liner with an acid-washed plastic spoon into acid-washed plastic bags for homogenization. Approximately 7 mL (1.5 g dry weight) was removed from the homogenized sample for P extraction. Approximately 5 mL was dedicated to the two-step extraction discussed here, and 2 mL was dedicated to additional extraction steps as part of a broader study. The remaining homogenized sediment was retained in the plastic bag for wet-weight dry-weight ratio (ww/dw), organic matter content via loss on ignition (LOI), and grain size analysis. For one core (the second location at the S site in spring), I sampled the

homogenized material twice to conduct replicate measurements of P and physical sediment properties. Replicate analyses are indicated with the label “S2-R.”

The ww/dw ratio was determined by first weighing the fresh, wet sediment (wet weight) and then allowing it to air dry for 24 hours. The sediment was then dried in an oven at 105 °C to constant weight (approximately 24 hours) and reweighed (dry weight). The ww/dw ratio was calculated by dividing the wet weight by the dry weight. Loss on ignition, a measure of the organic matter content in the sample, was determined by combusting samples at 550 °C for 4 hours. Specifically, LOI was calculated as:

$$100\% - (100 - \text{Weight in ash (g)}) / \text{Dry weight (g)}$$

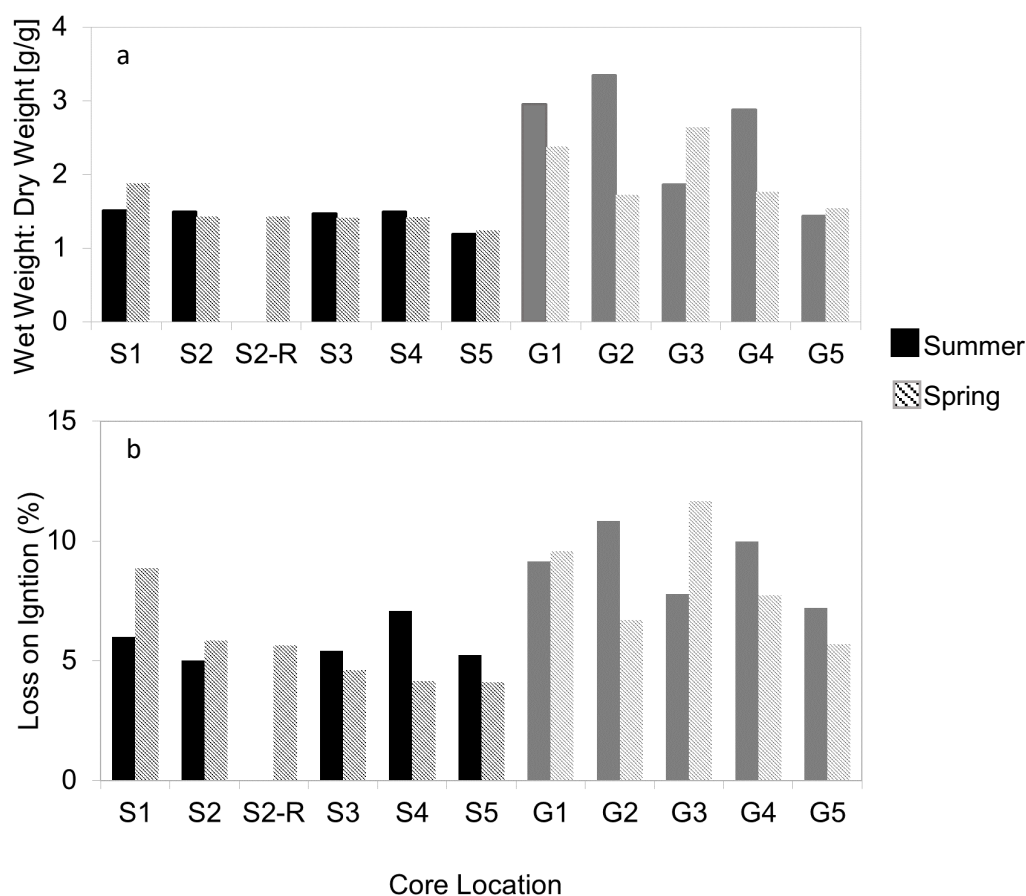
according to ASTM D 2974-87. Before conducting grain size analysis, samples were pretreated with 30% hydrogen peroxide solution to remove organic matter. Samples were then wet sieved to 63 µm, and the coarse fraction was dry sieved according to ASTM C136/C136M-14.

**Sequential Phosphorous Extraction.** Two extraction steps were used to determine loosely sorbed P and P bound to redox-sensitive Fe and Mn minerals (Paludan and Jensen, 1995; Kinsman-Costello et al., 2014). Briefly, loosely sorbed P (H<sub>2</sub>O-P) was isolated by rinsing the sample with Milli-Q water. Then, P bound to redox-sensitive Fe and Mn (BD-P) was isolated by rinsing the sample with 0.11 M bicarbonate dithionite solution. All samples were filtered to 45 µm, immediately refrigerated, and analyzed for SRP within 2 weeks following the ascorbic acid method (APHA, 1985). All P is reported as P-PO<sub>4</sub>.

## RESULTS

**Physical Sediment Properties.** The average ww/dw ratio at the G site was higher than the S site in both seasons (**Figure 4a**). The average ww/dw ratio was 2.252 g/g at G across both seasons and 1.451 g/g at S. There was no consistent change between summer 2017 and spring 2018: some cores showed an increase, while others showed a decrease (**Figure 4a**). Replicate ww/dw ratios for S2 site (S2-R) were similar (1.425 g/g and 1.429 g/g), indicating good reproducibility.

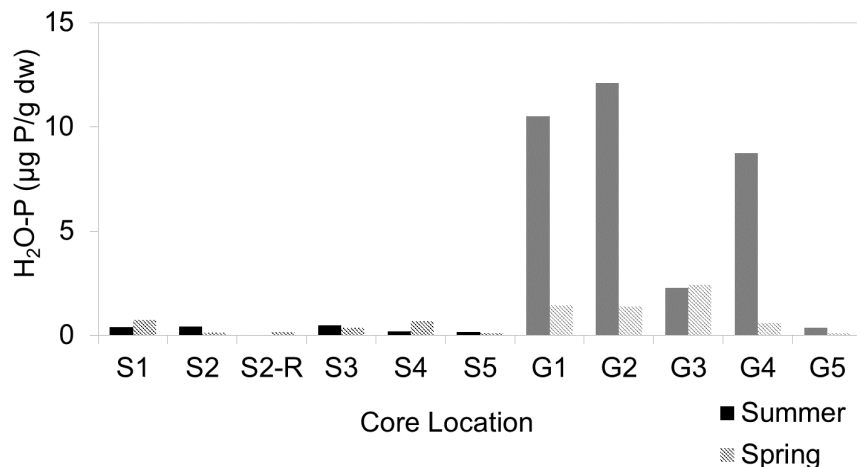
Organic matter content ranged from 4 to 12% across both sites and seasons (**Figure 4b**). Average values were 5.748% at the S site and 8.988% at the G site. Three locations showed an increase in organic matter content from summer 2017 to spring 2018 (S1, G1 and G3), while the others showed a decrease. In the three locations where organic matter increased, the ww/dw ratios also increased (**Figure 4**). Replicate organic matter content in the S2 site was similar (5.848% and 5.642%), again indicating good reproducibility.



**Figure 4.** a) ww/dw, a proxy for porosity, is plotted for each location at both sites and in both seasons (solid bars are summer and cross-hatched bars are spring).

b) Loss on Ignition, a proxy for the percentage of organic matter, is plotted for each location at both sites and in both seasons (solid bars are summer and cross-hatched bars are spring). Core locations are indicated in Figure 2.

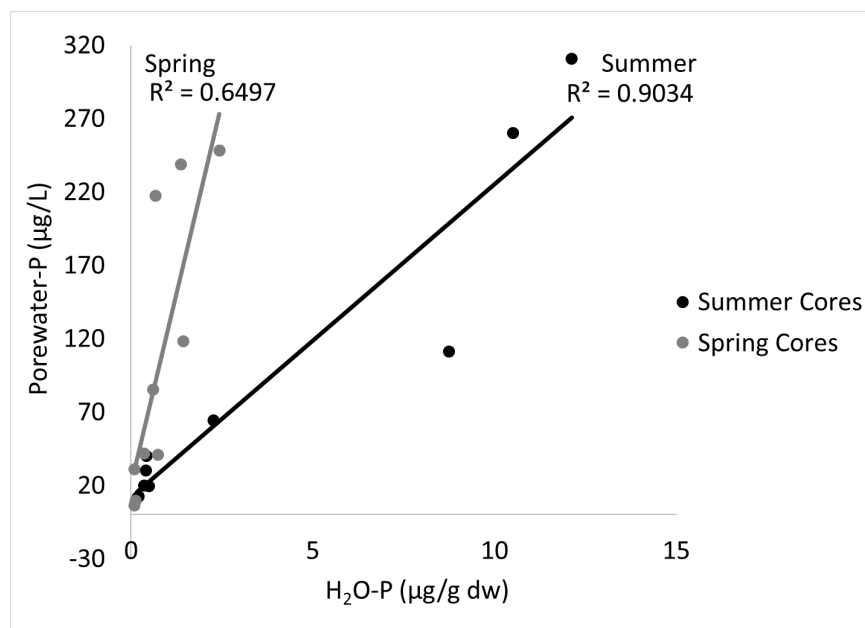
**Phosphorous Content.** Concentrations of loosely bound P ( $H_2O$ -P, the most mobile faction) were greater at the G site than the S site in both seasons (**Figure 5**). While the S site showed no strong seasonal variation, the G site had significantly greater concentrations in summer than spring. Average  $H_2O$ -P at the G site was  $6.80 \mu\text{g P/g dw}$  in summer 2017 and  $1.19 \mu\text{g P/g dw}$  in spring 2018.



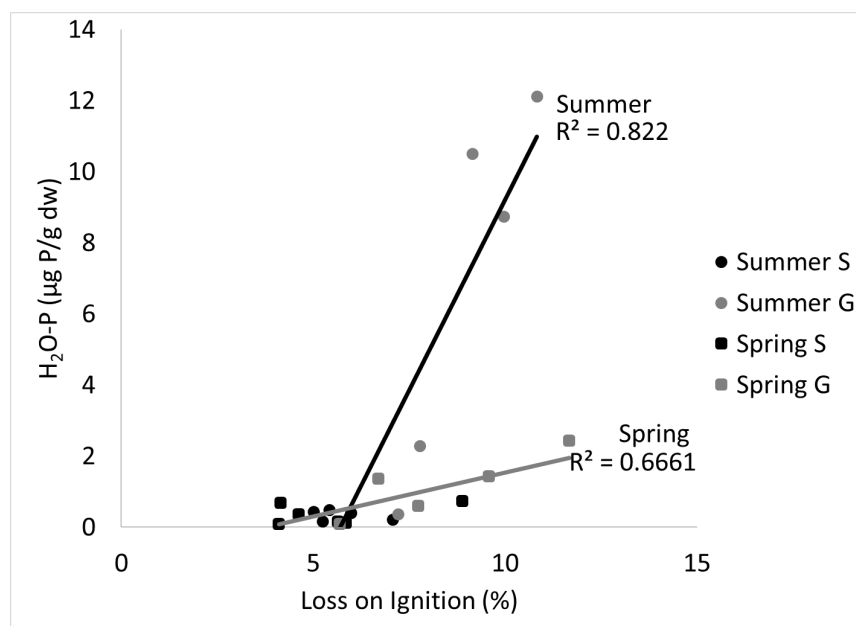
**Figure 5.** The concentration of loosely bound P ( $H_2O$ -P) is plotted for all locations and both seasons (solid bars are summer and cross-hatched bars are spring).

In both summer and spring, the cores with higher concentrations of the loosely bound P faction ( $H_2O$ -P) also had greater SRP concentrations in pore water extracted using Rhizon samplers, especially during the summer. This relationship is not surprising, since pore water collected with Rhizon samplers is probably similar to pore water collected in the water rinse step of the extraction process. Rhizon samplers may preferentially capture P from larger, more mobile pore spaces, but direct comparisons are difficult due to the different concentration units ( $\mu\text{g/g dw}$  versus  $\mu\text{g/L}$ ).

Loosely bound P ( $H_2O$ -P) tended to be greatest in cores with more organic matter (**Figure 8**). The correlation was particularly strong in summer.

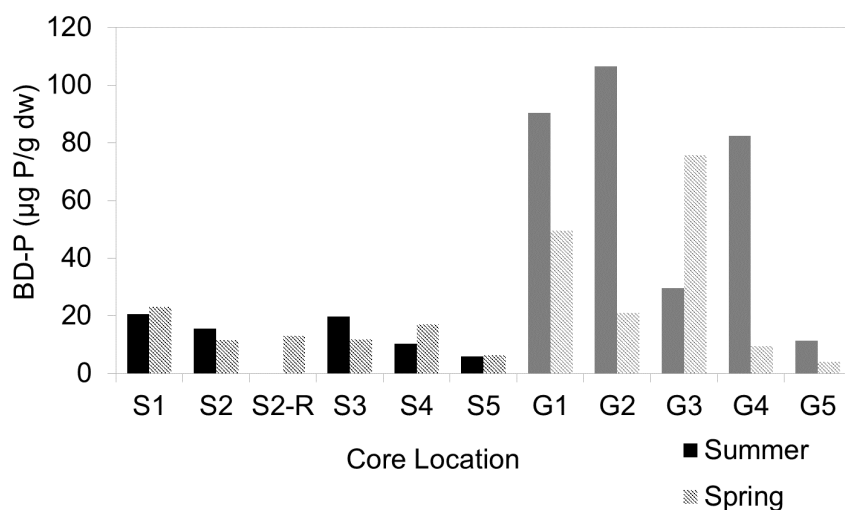


**Figure 5.** Porewater P from rhizon sampling during summer (black circles) and spring (grey circles) is plotted against loosely-bound H<sub>2</sub>O-P for each core location. The black line depicts the summer trend and the grey line depicts the spring trend. Respective Pearson correlation coefficients are shown above each trendline.



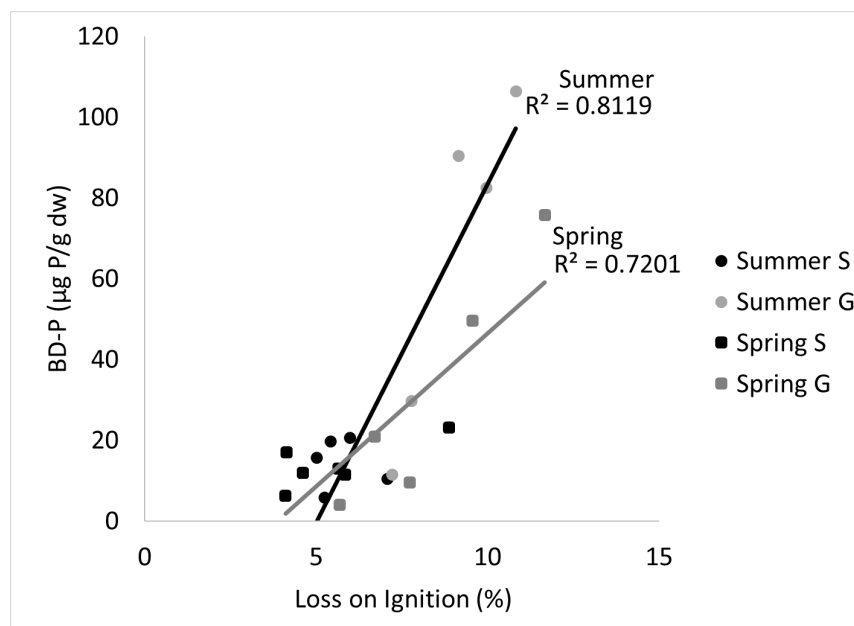
**Figure 6.** Loosely-bound H<sub>2</sub>O-P in summer (circles) and spring (squares) is plotted against the loss on ignition for all cores. The black line depicts the trend of all summer cores and the grey line depicts the trend of all spring cores. Respective Pearson correlation coefficients are shown above each trendline.

The concentration of P bound to redox-sensitive Fe/Mn (BD-P) was generally greater than H<sub>2</sub>O-P by a factor of 10 or more. BD-P was greater at the G site in both the spring and summer (**Figure 8**). Notably, the average summertime concentrations at the G site were elevated twice the average spring concentration (64.1  $\mu\text{g P/g dw}$  versus 32.0  $\mu\text{g P/g dw}$ ), while the concentrations at the S site remained nearly the same (14.4  $\mu\text{g P/g dw}$  versus 13.8  $\mu\text{g P/g dw}$ ), much like the H<sub>2</sub>O-P concentrations (**Figures 4 and 7**).



**Figure 7.** The concentration P bound to redox-sensitive Fe/Mn (BD-P) is plotted for all locations and both seasons (solid bars are summer and cross-hatched bars are spring).

The concentration of P bound to redox-sensitive Fe/Mn (BD-P) increased with organic matter content (**Figure 9**), similar to loosely bound P (**Figure 7**). Again, the correlation was strongest in the summer.



**Figure 8.** P bound to redox-sensitive Fe/Mn (BD-P) in summer (circles) and spring (squares) is plotted against the loss on ignition for all locations. The black line depicts the trend of all summer cores and the grey line depicts the trend of all spring cores. Respective Pearson correlation coefficients are shown above each trendline.



## DISCUSSION

The P content of sediments in agricultural drainage ditches showed large variations between and within farm sites, revealing multiple scales of spatial and seasonal variation. In both summer 2017 and spring 2018, P content (both H<sub>2</sub>O-P and BD-P) was almost always greater at the G site. However, at least one location there (G5) consistently had lower P content than some of the cores from S (**Figures 4-7**), showing that P content can vary widely within individual reaches over the scale of meters. Heterogeneity in sediment organic matter content can explain at least some of the meter-scale spatial variability in P content within sites (Dunne et. al., 2007) (**Figures 4-8**). Decomposition of local sediment organic matter may be a source of P that can remain dissolved in pore water (measured as pore water-P and H<sub>2</sub>O-P) or sorb to Fe and Mn oxides (measured as BD-P). Strong positive correlations between organic matter and P content in these different fractions were observed in both seasons, especially summer (Pearson correlation coefficients were 0.9034, 0.8220, and 0.8119 for pore water-P, H<sub>2</sub>O-P, and BD-P, respectively).

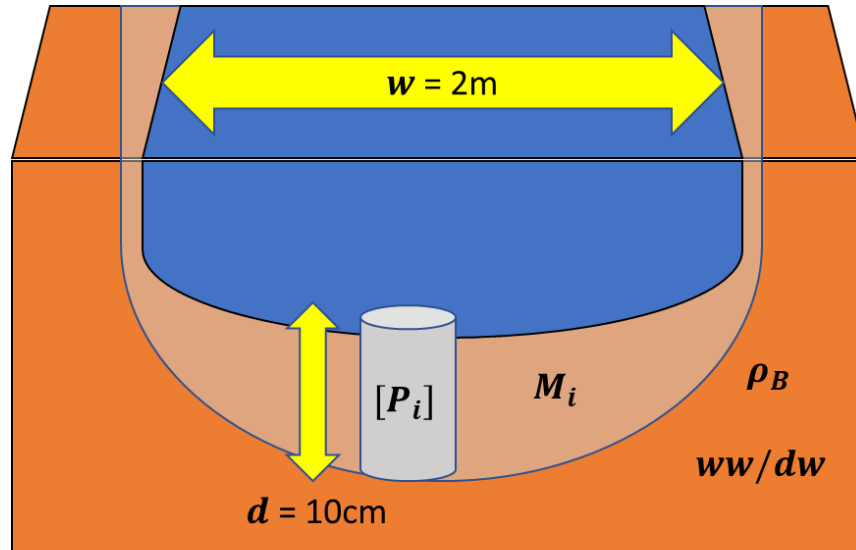
Variations in organic matter may also explain some of the large-scale variability in P content between the G and S sites. The G site had greater average organic matter content, likely due to differences in canopy shading and aquatic vegetation. Locally, the lack of well-developed tree canopies and shading at the G site allows dense aquatic vegetation to grow, which impedes flow and leads to more stagnant conditions in the channel. The stagnant water may allow for greater rates of sediment deposition and legacy P accumulation. Aquatic vegetation at the G site was so dense that stems and roots interfered with coring, and a pocket knife had to be used to cut vegetation around the bottom core cap to secure it. Dense vegetation in and around the drainage ditch helps prop open pore spaces, allowing greater ww/dw ratios, and is also a local source of dissolved P when it dies and decomposes. However, some of the S cores had similar organic matter content as the G cores and yet contained less P (e.g., S4 and S5 in **Figures 3,4, and 7**). Large-scale differences in P content between sites may also stem from differences in historical and current agricultural practices, both locally and upstream. A potential source would be fertilizer applications to upstream fields, along with other potential P inputs from livestock or towns within the catchment. For the scope of this in the ditch study, neither historical nor current data on fertilizer application were integrated but will be the focus of future investigations.

Seasonal fluctuations in P content may be influenced by external P inputs, mineralization of organic matter, and sorption-desorption processes that affect P exchange across the sediment-water interface. P exchange is partially controlled by the Fe-PO<sub>4</sub><sup>3-</sup> interaction on exposed sediments along the ditch perimeter. P retention occurs when P is adsorbed to oxidized iron minerals (Fe III). When oxygen is depleted in surface water, microbial activity reduces iron (Fe II) which leads to P desorption at the interface and delivery to surface waters (Kinsman-Costello, 2016). The concentration of the P bound to redox-sensitive metal oxides was generally an order of magnitude greater than the loosely sorbed P fraction, indicating that sediments could become a source of P if reducing conditions develop. Porewater P, loosely bound P, and P bound to redox-sensitive Fe/Mn were much greater in the summertime than in the springtime at the G site. This seasonal variation may be due at least partially to oxidation-reduction conditions near the sediment-water interface. That is, in the late summer conditions where stagnant flow was favored, reducing conditions may have promoted desorption of P from iron oxides. However, dissolved Fe in pore water samples was not measured. No strong seasonal variation was observed in S site, but this site was less choked with vegetation in summer and may have remained more oxic.

To assess the potential significance of the legacy P pool in shallow ditch sediments, I estimated average masses of relatively mobile P per linear meter of agricultural drainage ditch:

$$M_i = wd \frac{\rho_B}{ww/dw} [P_i],$$

where  $M_i$  is the mass of P per length of ditch [g/m] associated with extraction step  $i$  in a given season;  $w$  is the width of the drainage ditch [m];  $d$  is the thickness of unconsolidated ditch sediments [m];  $\rho_B$  is saturated sediment bulk density [g/m<sup>3</sup>];  $ww/dw$  is the seasonal average  $ww/dw$  ratio [g/g]; and  $[P_i]$  is the seasonally averaged concentration of P in the sediments (H<sub>2</sub>O-P or BD-P) [g/g dw]. I assumed  $w$  is 2 m and  $d$  is 0.1 m (a conservative estimate of the depth of refusal at both sites).  $\rho_B$  is calculated from a density of water of 1.0 g/m<sup>3</sup>, a density of soil of 1.6 g/m<sup>3</sup>, and an assumed porosity of 0.4



**Figure 10.** Schematic diagram of agricultural drainage ditch for calculating mobile P in unconsolidated ditch sediments (see Equation).

Table 1. Estimated mass of P in unconsolidated sediments per linear meter of drainage ditch.

	$M_{H_2O-P}$ (g/m)	$M_{BD-P}$ (g/m)	$M_{Total}$ (g/m)
<b>Spring</b>	0.0313	0.9359	0.9672
<b>Summer</b>	0.1454	1.5994	1.7448

To determine the total length of drainage ditches in the Cedar-Portage Watershed, ditches were identified using high-resolution hydrographic data from the National Hydrography Dataset, NHDPlus (McKay et al., 2012) for the Portage River watershed (HUC 04100010). Specifically, drainage ditches were assumed to include any reach mapped as a "drainage canal" and all first order reaches. The total length was 1,700 kilometers, which corresponds with a density of 0.681 km of ditch per square kilometer of watershed. If the average P content of the two sites in this study is representative of the entire watershed, then the mobile fraction of legacy P stored within ditches ranges from 1600 kg in spring to 3000 kg in summer (Table 2).

	$M_{H_2O-P}$ (kg)	$M_{BD-P}$ (kg)	$M_{Total}$ (kg)
<b>Spring</b>	58.50	1591.13	1649.62
<b>Summer</b>	247.21	2719.02	2966.23

These pools of mobile P are not insignificant in the context of P export from similar watersheds. For example, in the spring of 2012, the dissolved reactive P load from the Maumee River exported to Lake Erie was 63,000 kg (Ohio Lake Erie Phosphorous Task Force II, 2013).

It is unclear how rapidly P in ditch sediments may be exported. During low flows, P may slowly be released across the sediment-water interface due to advective and diffusive transport processes. During high flows, it is plausible that much more P is mobilized when unconsolidated sediments are suspended. In addition to the more mobile forms of P measured in this two-step extraction, relatively immobile forms of P can also be analyzed through additional extraction steps, including aluminum-bound P (NaOH-P), humic acid-bound P (Ha-P), iron colloidal-bound P (FeOx-P), and calcium-bound P (HCl-P). These fractions are currently being examined as part of a broader research effort, and the results will be important in addressing the individual and collective significance of all P stores in sediments.

## **CONCLUSIONS**

Sediments within drainage ditches contain substantial portions of relatively mobile P that may contribute to increasing dissolved P loads to Lake Erie. Concentrations of P associated with redox-sensitive metal oxides are approximately ten times greater than the loosely-sorbed fraction, indicating the importance of redox conditions near the sediment-water interface for mobilizing P from ditch sediments to surface waters. P concentrations are variable both in time and space. Sediments with more organic matter tended to have greater P concentrations over the scale of meters, but upstream land use and external P inputs may influence concentrations over the scale of kilometers. Analysis of upstream land use and fertilizer sales and application records are important directions for future research.

## **RECOMMENDATIONS FOR FUTURE WORK**

The elevated concentrations of mobile P at the G site in both seasons may be partially related to upstream land use and best management practices. Further investigation of land use data and fertilizer application records, such as the National Land Cover Database (NLCD) and county fertilizer records, would help test possible contributing factors for elevated P at the G site.

The timing of P release from ditch sediments and its fate within the watershed are unknown. A laboratory or combined laboratory-field study might attempt to determine how much of the P that can be extracted in the lab is mobilized in the field and over what timescales.

Complicating factors such as the highly variable discharge in the ditches and lack of flow records could make it difficult to track the fate of legacy P as it moves through the watershed. One potential method to quantify and identify relationships between legacy P in ditches and P export to Lake Erie might gauging stream flow and measuring P concentrations in ditches and smaller streams to create a mass budget for water and P. Another possible approach would be to conduct tracer injections of P in ditches and monitor downstream transport (e.g., Newbold et al., 1981).

## REFERENCES CITED

- Algoazany, A. S., Kalita, P. K., Czapar, G. F., and Mitchell, J. K., 2007, Phosphorus transport through subsurface drainage and surface runoff from a flat watershed in east central Illinois: *J. Environmental Quality*, v 36(3), p.681-693.
- APHA, 1985, *Standard Methods for the Examination of Water and Wastewater*, 16<sup>th</sup>: Washington, D.C.
- ASTM, D. 2974-87, 1993, *Standard test methods for moisture, ash, and organic matter of peat and other organic soils*: USA.
- ASTM. C136/C136M-14, 2014, *Standard Test Method for Sieve Analysis of Fine and Coarse Aggregates*: West Conshohocken, PA, ASTM International.
- Carlyle, G. C. and Hill, A. R., 2001, Groundwater phosphate dynamics in a river riparian zone: Effects of hydrologic flowpaths, lithology, and redox chemistry: *Journal of Hydrology*, v. 247, p.151-168.
- Dunne, E. J., J. Smith, D. B. Perkins, M. W. Clark, J. W. Jawitz, and K. R. Reddy, 2007, Phosphorus storages in historically isolated wetland ecosystems and surrounding pasture uplands: *Ecological Engineering* v.31, no. 1, p.16-28.
- Hendricks, S. P. and White, D. S., 2000, Streams and groundwater influences on phosphorus biogeochemistry: In *Streams and Groundwaters*: Waltham, MA, Academic Press, p. 221-235.
- Holman, I.P., Whelan, M. J., Howden, N. J. K., Bellamy, P., Willby, N., Rivas-Casado, M., and McConvey, P., 2008, Phosphorus in groundwater—an overlooked contributor to eutrophication?: *Hydrological Processes*, v. 22, p. 5121-5127.
- Hunter K. S., Wang Y., and Van Cappellen P., 1998, Kinetic modeling of microbially-driven redox chemistry of subsurface environments: coupling transport, microbial metabolism and geochemistry: *Journal of Hydrology*, v. 209, p. 53-80.
- International Joint Commission, 2014, *A Balanced Diet for Lake Erie: Reducing Phosphorus Loadings and Harmful Algal Blooms: Report of the Lake Erie Ecosystem Priority*.
- Jarvie, Helen P., Sharpley, Andrew N., Withers, Paul JA, Scott, J. Thad, Haggard, Brian E., and Neal, Colin, 2013, Phosphorus mitigation to control river eutrophication: Murky waters, inconvenient truths, and “postnormal” science: *Journal of Environmental Quality* v. 42, no. 2, p. 295-304.
- Jarvie, H. P., Sharpley, A. N., Spears, B., Buda, A. R., May, L., and Kleinman, P. J. A., 2013, Water quality remediation faces unprecedented challenges from “legacy phosphorus.”: *Environmental Science and Technology*, v. 47, p. 8997-8998.
- Kinsman-Costello, L. E., O'Brien, J., and Hamilton, S. K., 2014, Re-flooding a Historically Drained Wetland Leads to Rapid Sediment Phosphorus Release: *Ecosystems* v. 17, p. 641-656.
- Kinsman-Costello, Lauren E., Hamilton, Stephen K., O'Brien, Jonathan M., and Lennon, Jay T., 2016, Phosphorus release from the drying and reflooding of diverse shallow sediments: *Biogeochemistry* v. 130, no. 1-2, p. 159-176.

- McKay, L., Bondelid, T., Dewald, T., Johnston, J., Moore, R., and Rea, A., 2012, NHDplus v.2: user guide: [http://www.horizon-systems.com/NHDplus/NHDplusV2\\_home.php](http://www.horizon-systems.com/NHDplus/NHDplusV2_home.php).
- Michalak, A. M., Anderson, E. J., Beletsky, D., Boland, S., Bosch, N. S., Bridgeman, T. B., Chaffin, J. D., et al, 2013, Record-setting algal bloom in Lake Erie caused by agricultural and meteorological trends consistent with expected future conditions, in Proceedings, National Academy of Sciences, 201216006.
- Newbold, J. Denis, Elwood, Jerry W., O'Neill, Robert V., and Van Winkle, Webster, 1981, Measuring nutrient spiralling in streams: Canadian Journal of Fisheries and Aquatic Sciences, v.38, no. 7, p.860-863.
- Novak, J.M., Stone, K.C., Watts, D.W., and Johnson, M.H, 2003, Dissolved phosphorus transport during storm and base flow conditions from an agriculturally intensive south-eastern coastal plain watershed: Transactions of the ASAE, v. 46, p. 1355-1363.
- Ohio Environmental Protection Agency, 2015, Harmful algal blooms: Information for public water systems: Columbus, OH: <http://epa.ohio.gov/ddagw/HAB.aspx#114702844-basics>.
- Ohio Lake Erie Phosphorous Task Force II, 2013, Final Report: [https://lakeerie.ohio.gov/Portals/0/Reports/Task\\_Force\\_Report\\_October\\_2013.pdf](https://lakeerie.ohio.gov/Portals/0/Reports/Task_Force_Report_October_2013.pdf)
- Paludan, C. and Jensen, H., 1995, Sequential extraction of phosphorus in freshwater wetland and lake sediment: Significance of humic acids: Wetlands v. 15, p. 365-373.
- Penn, Chad, McGrath, Joshua, Bowen, James and Wilson, Stuart, 2014, Phosphorus removal structures: A management option for legacy phosphorus: Journal of Soil and Water Conservation, v. 69, no. 2, p. 51A-56A.
- Richards, R. P., Baker, D. B., Crumrine, J P., and Stearns, A. M., 2010, Unusually large loads in 2007 from the Maumee and Sandusky Rivers, tributaries to Lake Erie: Journal of Soil and Water Conservation, v.65, no. 6, p. 450-462.
- Sharpley, A., Jarvie, H. P., Buda, A., May, L., Spears, B., and Kleinman, P., 2013, Phosphorus legacy: overcoming the effects of past management practices to mitigate future water quality impairment: Journal of Environmental Quality, v. 42, no. 5, p. 1308-1326.
- Spiteri, C., Slomp, C. P., Regnier, P., Meile, C., and Van Cappellen, P., 2007, Modelling the geochemical fate and transport of wastewater-derived phosphorus in contrasting groundwater systems: Journal of contaminant hydrology, v.92, no. 1-2, p. 87-108.
- Shuttleworth, Sarah M., Davison, William, and Hamilton-Taylor, John, 1999, Two-dimensional and fine structure in the concentrations of iron and manganese in sediment pore-waters: Environmental Science and Technology, v. 33, no. 23, p. 4169-4175.

## APPENDIX

	Wet-weight dry-weight (g/g)		Loss on Ignition (%)		H <sub>2</sub> O-P [P-PO <sub>4</sub> ] (µg/g dw)		BD-P [P-PO <sub>4</sub> ] (µg/g dw)		Porewater-P [P-PO <sub>4</sub> ] (µg/L)	
Core	SU 2017	SP 2018	SU 2017	SP 2018	SU 2017	SP 2018	SU 2017	SP 2018	SU 2017	SP 2018
S1	1.506	1.882	5.991	8.877	0.402	0.737	20.5	23.1	30.3	41.1
S2	1.491	1.425	5.009	5.848	0.425	0.124	15.6	11.5	40.0	9.8
S2-R	-	1.430	-	5.642	-	0.169	-	13.0	-	-
S3	1.472	1.412	5.420	4.612	0.487	0.367	19.7	11.9	19.6	41.6
S4	1.494	1.423	7.075	4.143	0.208	0.682	10.4	17.0	12.4	217
S5	1.192	1.240	5.247	4.106	0.168	0.096	5.9	6.3	11.7	31.2
G1	2.956	2.378	9.154	9.566	10.5	1.43	90.3	49.6	260	118
G2	3.347	1.724	10.826	6.699	12.1	1.37	106	20.9	311	239
G3	1.860	2.637	7.778	11.67	2.28	2.43	29.7	75.7	64.4	248
G4	2.876	1.767	9.967	7.731	8.74	0.610	82.5	9.6	111	85.4
G5	1.438	1.540	7.215	5.681	0.364	0.095	11.4	4.1	20.0	6.2